

WHAT IS CLAIMED IS:

1. A silicone composition which can be crosslinked by dehydrogenative condensation, this composition comprising:

- 5 o -A- at least one organosiloxane monomer, oligomer and/or polymer having, per molecule, at least one reactive $\equiv\text{SiH}$ unit;
- o -B- at least one organosiloxane monomer, oligomer and/or polymer exhibiting, per molecule, at least one reactive $\equiv\text{SiOH}$ unit;
- 10 o -C- at least one catalytic complex;
- o -D- optionally at least one crosslinking inhibitor or retarder;
- o -E- optionally at least one polyorgano-
- 15 siloxane (POS) resin;
- o -F- optionally at least one filler;

characterized in that the catalytic complex -C- is an iridium complex capable of being obtained by reacting together:

- 20 -C1-, on the one hand, an iridium complex of formula (I):



in which:

1/ n is 1 or 2 and:

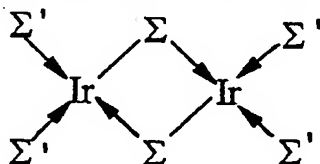
- 25 - if n is 1, Σ is a 3-electron radical ligand LX, preferably a ligand derived from acetylacetone, from a β -keto ester, from a malonic ester, from an allyl compound, from a carbamate, from a dithiocarbamate or from a carboxylic acid;
- 30 - if n is 2, Σ is a 1-electron radical ligand X which bridges the 2 iridium atoms, having a function of 1-electron ligand X for 1 iridium atom and of 3-electron ligand LX for the combination of the 2 iridium atoms, in particular a ligand chosen from halo, alkoxy or aryloxy;
- 35

2/ Σ' , which are identical or different, each represent a 2-electron ligand L chosen in particular

from: donors of a π bond pair, such as olefins, alkynes, C=O double bonds of an aldehyde or of a ketone, C=N or C=S; donors of a σ bond pair, such as H-H (dihydrogen) bonds or H-Si bonds, in particular in
5 silanes (H-SiR₃); and organophosphorus, R₂O, R₂S, NR₃ or THF ligands;

-C2-, on the other hand, a ligand Σ_d chosen from R₂S, R₂O, NR₃, carbenes or organophosphorus compounds of
10 formula P(OR)_p(R)_q with p and q ranging from 0 to 3, it being known that p+q = 3.

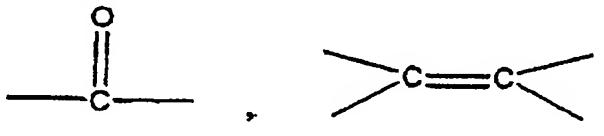
2. The composition as claimed in claim 1, characterized in that n=2 and the iridium complex is a dimeric complex of following formula (I'):



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in which:

- Σ is a 1-electron radical ligand X which bridges the 2 iridium atoms, having a function of 1-electron ligand X for 1 iridium atom and of
20 3-electron ligand LX for the combination of the 2 iridium atoms, in particular a ligand chosen from halo, alkoxy or aryloxy,
- Σ' are 2-electron ligands L formed of hydrocarbon groups comprising at least one unit



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preferably of hydrocarbon groups comprising the second unit, more preferably with the two Σ' ligands carried by the same Ir atom being carried by the same molecule.

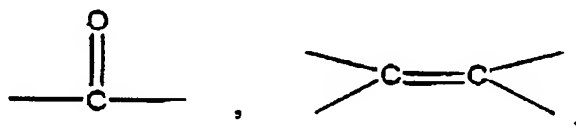
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3. The composition as claimed in claim 1, characterized in that n is 1 and Σ is chosen from the acetylacetonato, allyl, cyclopropenyl, carboxylato, carbamato or dithiocarbamato ligands, more particularly

the acetylacetonato and allyl ligands, preferably the acetylacetonato ligand.

4. The composition as claimed in claim 1 or 2, characterized in that n is 2 and Σ is a ligand chosen from halo, more particularly chloro, and alkoxy.

5. The composition as claimed in one of claims 1 to 4, characterized in that the Σ' ligands, which are identical or different, preferably identical, each represent a 2-electron ligand L chosen from hydrocarbon groups comprising at least one unit



the hydrocarbon groups being linear, branched, aromatic or (poly)cyclic, optionally interrupted by one or more heteroatoms (e.g., O, S or N) and comprising from 2 to 18 carbon atoms.

6. The composition as claimed in claim 5, characterized in that the two Σ' ligands bonded to the same Ir atom are functionalities carried by the same molecule.

7. The composition as claimed in claim 6, characterized in that this molecule is 1,5-cyclooctadiene.

8. The composition as claimed in one of claims 1 to 4, characterized in that the Σ' ligands are of $P(OR)_p(R)_q$ type with p and q ranging from 0 to 3, it being known that $p+q = 3$, preferably phosphines PR_3 and phosphites $P(OR)_3$.

9. The composition as claimed in one of the preceding claims, characterized in that the ligand Σ_a is an organophosphorus compound of formula $P(OR)_p(R)_q$ with p and q ranging from 0 to 3, it being known that $p+q = 3$, preferably a phosphine PR_3 or a phosphite $P(OR)_3$; in which formulae the R radicals, which are identical or different, are linear or branched alkyl radicals having in particular from 1 to 30 carbon atoms, preferably from 1 to 12 carbon atoms; alkyl

radicals comprising one or more rings, in particular 1 or 2 rings, it being possible for a ring to have in particular from 4 to 14 carbon atoms, preferably from 5 to 8 carbon atoms; or aryl or aralkyl radicals
5 comprising one or more fused or nonfused aromatic or heteroaromatic rings, in particular 1 or 2 rings, it being possible for a ring to comprise from 4 to 14 carbon atoms, preferably from 5 to 8 carbon atoms; the ring or rings are optionally substituted by one or more
10 groups, in particular from 1 to 2 groups, such as alkoxy, halide, amino or linear or branched alkyl having in particular from 1 to 12 carbon atoms, preferably from 4 to 12 carbon atoms.

10. The composition as claimed in one of
15 claims 1-2 and 4-9, characterized in that $n=2$ and the dimeric iridium complex is bis(1,5-cyclooctadiene)di-iridium(I) dichloride.

11. The composition as claimed in one of claims 1 to 10, characterized in that the ligand Σ_a is chosen
20 from the group consisting of triphenylphosphine and tris(para-methoxyphenyl)phosphine.

12. The composition as claimed in claim 1, characterized in that the catalytic complex -C- is the product of the mixing of bis(1,5-cyclooctadiene)di-
25 iridium(I) dichloride and of triphenylphosphine.

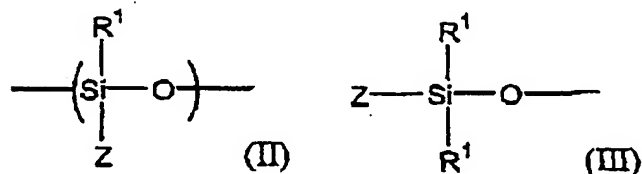
13. The composition as claimed in any one of the preceding claims, characterized in that it comprises from 1 ppm to 1000 ppm, preferably from 1 ppm to 300 ppm, of iridium metal with respect to the body
30 composed of the mixture of the oils possessing $\equiv\text{SiH}$ and $\equiv\text{SiOH}$.

14. The composition as claimed in any one of the preceding claims, characterized in that the catalytic complex employs from 0.5 to 10, especially from 0.5 to
35 5, more particularly from 0.5 to 2, mol of ligand Σ_a per 1 mol of Ir.

15. The composition as claimed in claim 14, characterized in that the catalytic complex employs from 0.75 to 1.5, in particular from 0.75 to 1.25 and

better still 1 mol of ligand Σ_d per 1 mol of Ir.

16. The composition as claimed in any one of the preceding claims, characterized in that the organo-siloxane monomers, oligomers and/or polymers -A-
 5 possessing reactive $\equiv\text{SiH}$ units have at least one unit of formula (II) and are terminated by units of formula (III) or are cyclic and are composed of units of formula (II) represented below:



10 in which:

- the symbols R^1 are identical or different and represent:

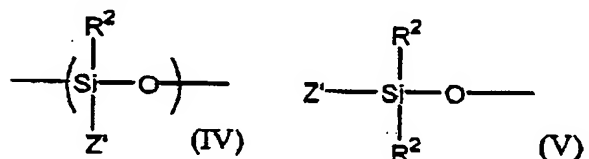
- a linear or branched alkyl radical comprising from 1 to 8 carbon atoms which is optionally substituted by at least one halogen, preferably fluorine, the alkyl radicals preferably being methyl, ethyl, propyl, octyl and 3,3,3-trifluoropropyl,
- an optionally substituted cycloalkyl radical comprising between 5 and 8 cyclic carbon atoms,
- an optionally substituted aryl radical comprising between 6 and 12 carbon atoms,
- an aralkyl radical having an alkyl part comprising between 5 and 14 carbon atoms and an aryl part comprising between 6 and 12 carbon atoms which is optionally substituted on the aryl part by halogens, alkyls and/or alkoxy groups comprising from 1 to 3 carbon atoms,

- the symbols Z are alike or different and represent:

- a hydrogen radical,
- a group corresponding to the same definition as that given above for R^1 ,

with, per molecule, at least one of the symbols Z representing H.

17. The composition as claimed in one of the preceding claims, characterized in that the organo-siloxane monomers, oligomers and/or polymers -B-possessing reactive $\equiv\text{SiOH}$ units have at least one unit of formula (IV) and are terminated by units of formula (V) or are cyclic and are composed of units of formula (IV) represented below:



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in which:

- the symbols R^2 are identical or different and represent:

- a linear or branched alkyl radical comprising from 1 to 8 carbon atoms which is optionally substituted by at least one halogen, preferably fluorine, the alkyl radicals preferably being methyl, ethyl, propyl, octyl and 3,3,3-trifluoropropyl,
- an optionally substituted cycloalkyl radical comprising between 5 and 8 cyclic carbon atoms,
- an optionally substituted aryl radical comprising between 6 and 12 carbon atoms,
- an aralkyl radical having an alkyl part comprising between 5 and 14 carbon atoms and an aryl part comprising between 6 and 12 carbon atoms which is optionally substituted on the aryl part by halogens, alkyls and/or alkoxy groups comprising from 1 to 3 carbon atoms,

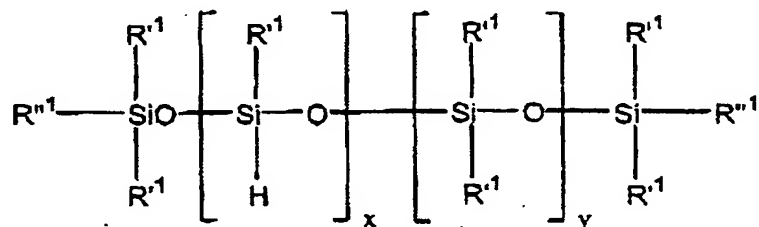
- the symbols Z' are alike or different and represent:

- a hydroxyl group,
- a group corresponding to the same definition

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as that given above for R^2 ,
with, per molecule, at least one of the symbols Z'
representing OH.

18. The composition as claimed in one of the
preceding claims, characterized in that the organo-
siloxane monomers, oligomers or polymers -A- possessing
reactive $\equiv SiH$ units correspond to the general
formula (VI):



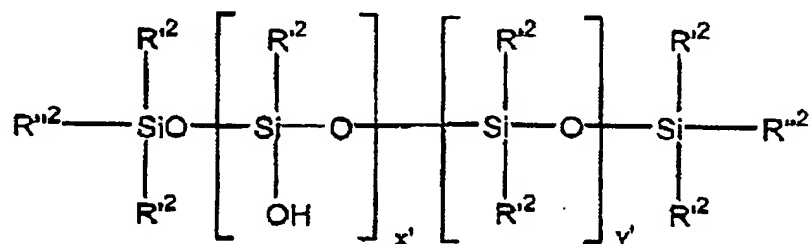
in which:

- x and y each represent an integer or fractional number varying between 0 and 200,
- R'^1 and R''^1 represent, independently of one another:

- a linear or branched alkyl radical comprising from 1 to 8 carbon atoms which is optionally substituted by at least one halogen, preferably fluorine, the alkyl radicals preferably being methyl, ethyl, propyl, octyl and 3,3,3-trifluoropropyl,
- an optionally substituted cycloalkyl radical comprising between 5 and 8 cyclic carbon atoms,
- an optionally substituted aryl radical comprising between 6 and 12 carbon atoms,
- an aralkyl radical having an alkyl part comprising between 5 and 14 carbon atoms and an aryl part comprising between 6 and 12 carbon atoms which is optionally substituted on the aryl part,

- it being possible for R''^1 also to correspond to hydrogen, with the condition according to which at least one of the R'^1 radicals (preferably both) correspond to hydrogen when $x = 0$.

19. The composition as claimed in one of the preceding claims, characterized in that the organo-siloxane monomers, oligomers or polymers -B- possessing reactive $\equiv\text{SiOH}$ units correspond to the general formula (VII):



in which:

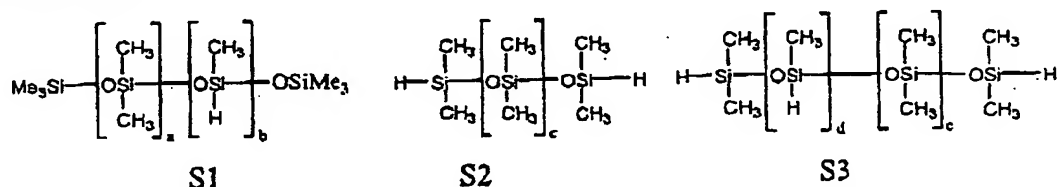
- x' and y' each represent an integer or fractional number varying between 0 and 1200,
- R'^2 and R''^2 represent, independently of one another:
 - a linear or branched alkyl radical comprising from 1 to 8 carbon atoms which is optionally substituted by at least one halogen, preferably fluorine, the alkyl radicals preferably being methyl, ethyl, propyl, octyl and 3,3,3-trifluoropropyl,
 - an optionally substituted cycloalkyl radical comprising between 5 and 8 cyclic carbon atoms,
 - an optionally substituted aryl radical comprising between 6 and 12 carbon atoms,
 - an aralkyl radical having an alkyl part comprising between 5 and 14 carbon atoms and an aryl part comprising between 6 and 12 carbon atoms which is optionally substituted on the aryl part,
- it being possible for R''^2 also to correspond to OH, with the condition according to which at least one of the R''^2 radicals (preferably both) correspond to OH when $x' = 0$.

20. The composition as claimed in one of the preceding claims, characterized in that the organo-siloxane monomers, oligomers or polymers possessing

reactive $\equiv\text{SiH}$ units comprise from 1 to 50 active $\equiv\text{SiH}$ units per molecule.

21. The composition as claimed in one of the preceding claims, characterized in that the organo-siloxane monomers, oligomers or polymers possessing reactive $\equiv\text{SiOH}$ units comprise from 1 to 50 active $\equiv\text{SiOH}$ units per molecule.

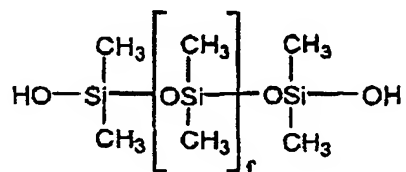
22. The composition as claimed in one of the preceding claims, characterized in that the organo-siloxane monomers, oligomers or polymers -A- possessing reactive $\equiv\text{SiH}$ units are chosen from the compounds of formulae:



with a, b, c, d and e representing a number varying from:

- in the polymer of formula S1:
 $0 \leq a \leq 150$, preferably $0 \leq a \leq 100$, preferably $0 \leq a \leq 20$, and
 $1 \leq b \leq 55$, preferably $10 \leq b \leq 55$, preferably $30 \leq b \leq 55$,
- in the polymer of formula S2:
 $0 \leq c \leq 15$,
- in the polymer of formula S3:
 $5 \leq d \leq 200$, preferably $20 \leq d \leq 50$, and
 $2 \leq e \leq 50$, preferably $10 \leq e \leq 30$.

23. The composition as claimed in one of the preceding claims, characterized in that the organo-siloxane monomers, oligomers or polymers -B- possessing reactive $\equiv\text{SiOH}$ units are chosen from the compounds of formula:



S4

with $1 \leq f \leq 1200$, preferably $50 \leq f \leq 400$, preferably $150 \leq f \leq 250$.

24. The composition as claimed in one of the preceding claims, characterized in that the $\equiv\text{SiH}/\equiv\text{SiOH}$ ratio is between 1 and 100, preferably between 10 and 50 and more preferably still between 15 and 45.

25. A process for polymerizing and/or crosslinking a composition as claimed in any one of the preceding claims, characterized in that a dehydrogenative condensation is carried out between said compounds -A- and -B- and in that said dehydrogenative condensation is initiated by thermal activation of the catalytic complex -C-.

26. A process for producing at least one release coating on a support, preferably a flexible support, characterized in that it comprises the application, to this support, of a composition as claimed in any one of claims 1 to 24 and then ensuring that crosslinking occurs.

27. A process for producing at least one article made of crosslinked silicone foam, characterized in that it comprises applying, to this support, a composition as claimed in any one of claims 1 to 24 and then ensuring that crosslinking occurs.

28. A coating, obtained by crosslinking a composition as claimed in any one of claims 1 to 24.

29. An article composed of a solid material, at least one surface of which is coated with a coating as claimed in claim 28.

30. A crosslinked silicone foam, obtained by crosslinking a composition as claimed in any one of claims 1 to 24.

31. A process for the preparation of a branched polyorganosiloxane comprising at least two polyorganosiloxane chains connected to one another via an Si-O-Si siloxyl group in which a dehydrogenative condensation reaction is carried out between an organosiloxane monomer, oligomer or polymer A' comprising reactive $\equiv\text{SiH}$ units and an organosiloxane

monomer, oligomer or polymer B' comprising reactive $\equiv\text{SiOH}$ units, characterized in that said dehydrogenative condensation reaction is carried out in the presence of the catalytic complex C defined according to one of
5 claims 1 to 15 and is optionally initiated by thermal activation.

32. The process for the preparation of a branched polyorganosiloxane as claimed in claim 31, in which the $\equiv\text{SiH}/\equiv\text{SiOH}$ ratio is greater than 1.